(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(54) Title: A POLYMER GEL HYBRID SOLAR CELL

WO 03/054894 A1

- substrate
- back-electrode
- polymer gel electrolyte + redox-couple
- dye sensitised porous TiO₂
- blocking layer
- FTO
- substrate
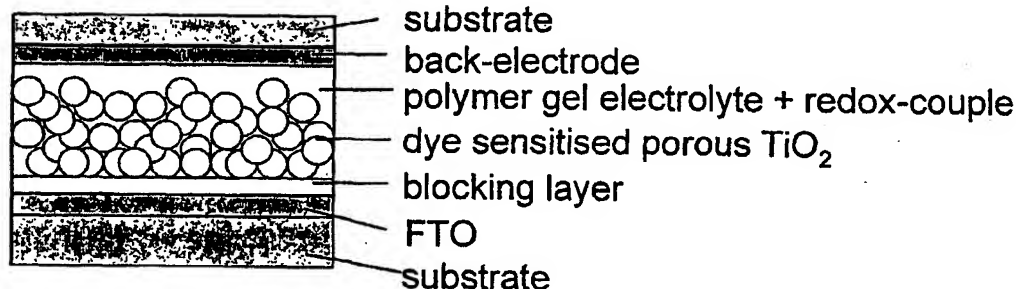
(57) Abstract: The invention relates to a polymer gel hybrid solar cell. In particular, cells are disclosed which reach a light to energy conversion efficiency as high as 9.2 % with 100 mW/cm², and as high as 14.1 % with reduced light intensity of 33 mW/cm².

A polymer gel hybrid solar cell

The invention relates to a polymer gel hybrid solar cell comprising a polymer gel electrolyte.

Single crystal solar cells show energy conversion efficiencies as high as ~ 25%. Where the Si-based crystals are no longer single crystals but polycrystalline, the highest efficiencies are in the range of ~18%, and with amorphous Si the efficiencies are ~12%. Solar cells based on Si are, however, rather expensive to manufacture, even in the amorphous Si version.

Therefore alternatives have been developed based on organic compounds and/or a mixture of organic and inorganic compounds, the latter type solar cells often being referred to as hybrid solar cells. Organic and hybrid solar cells have proved to be cheaper to manufacture, but seem to have yet comparably low efficiencies even when compared to amorphous Si cells.

Due to their inherent advantages such as lightweight, low-cost fabrication of large areas, earth-friendly materials, or preparation on flexible substrates, efficient organic devices might prove to be technically and commercially useful 'plastic solar cells'. Recent progress in solar cells based on dye-sensitised nanocrystalline titanium dioxide (porous TiO_2) semiconductor and a liquid redox electrolyte demonstrates the possibility of high energy conversion efficiencies in organic materials (η 11%) [B. O'Regan and M. Grätzel, Nature 353 (1991) 737; data base: Keycentre for Photovoltaic Engineering UNSW]. The basic structure of the hybrid solar cell is illustrated in figure 1.

However, for these solar cells to become widely used, there are still a number of drawbacks to overcome, namely the use of liquid electrolytes for charge transport. Ideally, solid electrolytes should be used to eliminate the possibility of electrolyte leakage in long-term operation, and to eliminate the difficulties in production steps such as injection and sealing of the electrolyte solution. Furthermore, restriction in design of the cell should be reduced, and any shape should be available such as a cylindrical-shape cell, flexible cell, and so on. Nonetheless, the efficiencies of solid-state organic solar cells based on solid-state hole transport materials are low in comparison to the liquid ones (up to 2.5%) [a) Krueger et al., Appl. Phys. Lett. 79, p. 2085 (2001); b) results obtained by present inventors (not shown)], because of the incomplete

penetration of hole transport material into, and the detachment of the hole transport layer from, the TiO_2 electrode [S. Tanaka, Japanese Journal of Applied Physics, 40 (2001) 97].

To address those problems, attention is increasingly focusing on developing "quasi solid state" electrolytes, to combine the high efficiency of the liquid cell with the advantages of the solid state cell. There are reports about the addition of polymeric gelling agents in the liquid electrolyte to promote solidification, and about polymer gel electrolytes [M. Matsumoto, H. Miyazaki, K. Matsuhiro, Y. Kumashiro and Y. Takaoka, Solid State Ionics 89 (1996) 263. S. Mikoshiba, H. Sumino, M. Yonetsu and S. Hayase, Proceedings of the 16th European Photo-voltaic Solar Energy Conference and Exhibition, Glasgow 2000. W. Kubo, K. Murakoshi, T. Kitamura, Y. Wada, K. Hanabusa, H. Shirai, and S. Yanagida, Chemistry Letters (1998) 1241. A. F. Nogueira, J. R. Durrant, and M. A. De Paoli, Advanced Materials 13 (2001) 826.] There are, however, also problems associated with this approach, since for the formation of suitable gels, some requirements have to be fulfilled such as amorphous character, high melt-ing, etc. Classical gels contain 10% gelator, which in turn decreases the conductivity and the interface contact. Furthermore, many gels cannot be formed in the presence of iodine (which is often part of the redox couple present in the cell), since this is a radical cation catcher. Also some iodides form complexes with the monomers which prevents them from polymerization. This limits the nature of components and the polymerisation techniques to be chosen for forming a chemically cross-linked gel.

Therefore it has been an object of the present invention to avoid the problems described in relation to polymer gel electrolyte solar cells. It has further been an object to provide a hybrid solar cell which has a high energy conversion efficiency. It has also been an object to provide a hybrid solar cell which can be formed into a variety of shapes.

The object is solved by a polymer gel hybrid solar cell comprising a polymer gel electrolyte, wherein the polymer gel electrolyte comprises a polymer, selected from the group comprising homopolymers and copolymers.

Preferably, the homopolymer is linear or non-linear.

In one embodiment, the copolymer is selected from the group comprising statistical copoly-mers, random copolymers, alternating copolymers, block-copolymers and graft copolymers.

In a preferred embodiment, the polymer is a linear polymer.

More preferably, the polymer is crosslinked.

Preferably, the polymer is not covalently crosslinked.

It is preferred that the polymer is physically crosslinked.

In one embodiment, the polymer has a $M_w > 90,000$, preferably a $M_w > 200,000$, more preferably a $M_w > 400,000$.

In one embodiment the polymer is a polyethylene oxide or a derivative thereof.

In a preferred embodiment, the polymer constitutes $1 - 10$ wt% of the polymer gel electrolyte, preferably $1 - 5$ wt% of the polymer gel electrolyte.
In a particularly preferred embodiment the polymer constitutes ~3 wt.% of the polymer gel electrolyte.

In one embodiment, the polymer gel electrolyte has an ionic conductivity $> 1 \times 10^{-6}$ S/cm, preferably $> 1 \times 10^{-4}$ S/cm, these values being measured without a redox couple being present in the polymer gel electrolytye. In a particularly preferred embodiment the ionic conductivity is $> 1 \times 10^{-3}$ S/cm.

It is preferred that the polymer gel electrolyte further comprises a base and/or a radical scavenger and/or a complexing agent and/or a pinhole-filler and/or a compound reducing the charge recombination.

In one embodiment, the polymer gel electrolyte further comprises an amine. Preferably the amine is a pyridine or a pyridine derivative selected from the group comprising pyridine, 4-tert-butylpyridine, 2-vinylpyridine, and poly(2-vinylpyridine).

In one embodiment the base/radical scavenger/ complexing agent/pinhole-filler/compound reducing the charge recombination is a compound selected from the group comprising com-

pounds having one or several carboxy groups, compounds having one or several amine groups, compounds having one or several carboxy and one or several amine groups, compounds having free electron lone pairs.

Preferably, the polymer gel electrolyte further comprises a redox couple, wherein it is preferred that the redox couple has a low probability to perform recombination reactions with electrons injected into the negatively charged molecules of the electron transport layer (which can be e.g. porous TiO_2). Preferably the redox couple has a redox potential so it cannot be oxidised or reduced by the working electrode. More preferably, the redox couple is I^-/I_3^-.

In a preferred embodiment, the redox couple is I^-/I_3^- with the counterion C of I^- being selected from the group comprising Li, Na, K, tetrabutylammonium, Cs and DMPII (molten salt) (1-propyl-2,3-dimethylimidazolium iodide ($C_8H_{15}N_2I$).

It is preferred, that the polymer gel electrolyte further comprises a salt, wherein, preferably, the salt is a redox inert salt which, even more preferably, is $Li(CF_3SO_2)_2N$.

It is preferred that the polymer gel electrolyte further comprises at least one solvent selected from the group comprising propylene carbonate, ethylene carbonate, dimethyl carbonate and acetonitrile. It is to be understood that the solvent is not restricted to the aforementioned ones. One characterising feature of a solvent suitable for the purposes of the present invention is the high permittivity, which supports the dissociation of the components of the redox agent (e.g. iodide).

In one embodiment, the polymer gel electrolyte is ionically and/or electronically conductive.

Preferably, the polymer gel electrolyte is selected from the group comprising:
- polyethylene oxide, $LiClO_4$, propylene carbonate and/or ethylene carbonate,
- polyethylene oxide, NH_4ClO_4, propylene carbonate and/or ethylene carbonate,
- polyethylene oxide and/or polymethylmethacrylate, $LiClO_4$, propylene carbonate and/or ethylene carbonate,
- polyacrylonitrile, Li- and/or Mg trifluoromethanesulfonate, propylene carbonate and/or ethylene carbonate,
- polyethylene oxide and poly(2-vinylpyridine), $LiClO_4$, 7,7,8,8-tetracyano-1,4-

quinodimethane (TCNQ) and/or tetracyanoethylene (TCNE),
- polyethylene oxide and polyaniline, $Li(CF_3SO_2)_2N$ and $H(CF_3SO_2)_2N$,
- polyaniline grafted with poly(ethyleneoxy)carboxylate,
- polyethylene oxide and poly(3,4-ethylenedioxythiophene)-polystyrenesulfonate
  (PEDOT-PSS).

Preferably, the polymer gel hybrid solar cell is dye-sensitised.

In one embodiment, the dye is a ruthenium complex, preferably cis-di(thiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylate)ruthenium(II)tetrabutylammonium (Ru(bpy)TBA).

Preferably, the polymer gel electrolyte further comprises nanoparticles, wherein, more preferably, the nanoparticles have an average size in the range from 2 nm - 25 nm.

In one embodiment, the nanoparticles are formed of a semiconductor material.

In one embodiment, the nanoparticles are formed of a material selected from the group comprising TiO_2, ZnO, SnO_2, PbO, WO_3, Fe_2O_3, Bi_2O_3, Sb_2O_3, Nb_2O_5, Ta_2O_5, SrO_2.

In one embodiment the semiconductor nanoparticles are admixed with Au- and/or Ag-nanoparticles.

The object of the invention is also solved by an array of polymer gel hybrid solar cells according to the present invention.

As used herein, the expression "not chemically crosslinked" is used interchangeably with "not covalently crosslinked" and is meant to designate the absence of covalent crosslinking bonds. The term "a polymer is physically crosslinked" is meant to designate a polymer the crosslinking of which between polymer molecules is based on mainly non-covalent interactions, e.g. van der Waals-interactions, hydrophobic interactions, etc.

As used herein the term "homopolymer" is meant to designate a polymer which is derived from one species of monomer. If "A" denotes such a monomer, a homopolymer would be "-A-A-A-A-A..." or $-[A]_n-$, with n indicating the number of repeating units (or monomer units) that are linked together. As used herein, the term "copolymer" is meant to designate a polymer derived from more than one species of monomer. As used herein the term "linear" polymer is meant to designate a polymer that essentially has one chain of monomers linked to-

gether and furthermore has only two ends. The term "linear", however, can also be applied to individual regions of a polymer, which then means that such a linear region essentially consists of a chain with two ends. As used herein, the term "non-linear" polymer is meant to designate any polymer that is not linear in the aforementioned sense. In particular, it refers to polymers which are branched polymers, or polymers which are dendritic. As used herein, the term "branched" polymer is meant to designate a polymer having sidechains or branches which are bonded to the main chain at specific branch points. Furthermore the term "non-linear" polymer is also meant to designate "network polymers", which are polymers having a three-dimensional structure in which each chain and/or branch is connected to all other chains and/or branches by a sequence of junction points and other chains/branches. Such network polymers are also sometimes referred to as being "crosslinked", and they are characterized by their crosslink density or degree of crosslinking, which is the number of junction points per unit volume. Usually they are formed by polymerization or by linking together pre-existing linear chains, a process also sometimes referred to as "crosslinking". Furthermore the term "non-linear" polymer also refers to dendritic polymers which are polymers obtained by a process wherein, in each step two or more monomers are linked to each monomer that is already part of the growing polymer molecule. By such a process, in each step, the number of monomer-endgroups grows exponentially, and the resulting structure is a tree-like structure showing a typical "dendritic" pattern.

As used herein, the term "statistical" copolymer is meant to designate a copolymer wherein the sequential distribution of repeating units or monomers obeys known statistical laws. The term "random" copolymer is meant to designate a special type of statistical copolymers wherein the distribution of repeating units or monomers is truly random. More specifically, the term "random" copolymer can designate a specific type of statistical copolymers wherein the sequential distribution of the monomers obeys Bernoullian statistics. As used herein, the term "alternating" copolymer is meant to designate a polymer, wherein different types of repeating units are arranged alternately along the polymer chain. For example, if there are only two different types of monomers, "A" and "B", the alternating copolymer would be "...ABABABAB...". If there are three different types of monomers, "A", "B" and "C", the alternating copolymer would be "...ABCABCABC...". The term "block" copolymer is meant to designate a copolymer wherein there are different blocks each of which is formed of one type of monomer, and which copolymer can be described by the sequence of blocks. For example if one type of block is formed by the monomer "A" and the other type of block is

formed by the monomer "B", a block copolymer thereof can be described by the general formula ...-A_k-B_l-A_m-B_n-...; k, l, m and n designating the number of monomers in each block. As used herein, the term "graft" polymers is meant to designate branched polymers, which, along their main chain, have side chains with such a length that these side chains can be referred to as polymers themselves. The side chains and the main chain can be chemically identical or different to each other. If they are chemically identical, they are also referred to as "graft polymers", whereas, if they are different to each others, they are referred to as "graft copolymers". The branches and the main chain may be formed of different homopolymers, or each of them, i. e. the branches and the main chain may be formed of different monomers, such that each of them is a copolymer itself.

In the following specific description reference is made to the figures, wherein

Figure 1 shows the basic structure of a hybrid solar cell having I^-/I_3^- as redox couple and a TiO_2 layer as electron transport layer,

Figure 2 shows the electron transfer and transport processes taking place in such a cell,

Figure 2A shows the same processes in a different representation using energy levels,

Figure 3 shows the I/V-curve of a PEO containing hybrid solar cell with 10 nm particle size, 7 µm porous TiO_2 layer thickness,

Figure 4 shows the I/V-curve of PEO plus tert-butylpyridine containing hybrid solar cell, 10 nm particle size, 4 µm porous TiO_2 layer thickness, and

Figure 5 shows the I/V-curves of PEO plus tert-butylpyridine containing hybrid solar cell, 20 nm particle size, 9 µm porous TiO_2 layer thickness, and

Figure 6 shows the I/V-curves of a PEO plus tert-butylpyridine containing hybrid solar cell, 20 nm particle size, 9µm porous TiO_2 layer, and

Figure 6A shows the energy conversion efficiency plotted versus light intensity of the solar cell of figure 6.

The following examples are intended to describe the invention more specifically by way of example and are not intended to limit the scope or spirit of the invention.

Example 1

In one example, polyethylene oxide [PEO, M_w 400.000] was used in ethylene carbonate [EC]

/ propylene carbonate [PC] mixture filled with lithium iodide / iodine [LiI/I$_2$] and an inert Li salt. In PEO polymer gel electrolyte, the solid polymer matrix of PEO provides dimensional stability to the electrolyte, while the high permittivity of the solvents PC and EC enables extensive dissociation of the Li salts to take place. The low viscosity of PC and EC provides an ionic environment that facilitates high ionic mobility. Such polymer gel electrolytes exhibits high ionic conductivities in excess of 10^3 S/cm.

Example 2

Solar cell preparation

Blocking layer

Made by spray pyrolysis: spraying with an atomiser an aerosol dispersion of an organic precursor titanium acetylacetonate (TAA, Aldrich) in ethanol (concentration of 0.2 M) onto structured FTO coated glass substrates (at 450°C) (Geomatic). To get a thin, amorphous, compact layer of TiO$_2$ (about 30 nm), films are tempered at 500°C in air for 1 hour.

Nanocrystalline TiO$_2$ electrode + dye layer

Porous TiO$_2$ layers are made by screen printing of a paste containing TiO$_2$ particle of 10 nm or 20 nm diameter respectively (Solaronix Company) on top of the blocking TiO$_2$ layer (thickness depends on mesh size of screens). To get rid of the organic solvents and surfacatants, and to enable a contact between TiO$_2$ particles, porous TiO$_2$ layers are heated up to 85°C for 30 minutes in a first step and sintered at 450°C for ½ hour. After cooling down to 80°C, films are placed into a dye solution in ethanol (5 x 10^{-4} M) and stay there overnight in the dark. Afterwards, substrates are rinsed with ethanol and dried several hours in the dark.

Polymer gel electrolyte

PEO (MW 400.000) was dissolved in THF (30mg/3ml) and stirred with heating up to 75°C for 10 min, cooling down to room temperature. I$_2$ and LiI (ratio 1:10 by weight; 4.4 mg I$_2$ (5.7 mM), 44 mg LiI (0.1M)) were dissolved in 0.5 ml THF and mixed with PC/EC (ratio 1:1 by weight, 1 g). Furthermore, bistrifluoromethane sulfonimide lithium (Li((CF$_3$SO$_2$)$_2$N)) was added to the mixture (9.6 mg (7.8 mM)), this concentration yields to an EO:Li ratio of 20:1. Both solutions were mixed in a next step, 50µl were drop casted on top of the dyed porous TiO$_2$ electrode and kept over night in the dark to allow the evaporation of THF. If applied, tert.-butylpyridine is added to the gel, or the dye-sensitised substrate were placed into a 50% solution in acetonitrile for 15 min before drop casting the polymer electrolyte.

Back-electrode

Platinum coated FTO substrate (Geomatic) was placed on top as backelectrode to form a sandwich with defined distance of 6 µl (PS foil).

Measurements

Photocurrent-voltage characteristic

Photochemical measurements were done using a potentiostat (EG&G Princeton applied research, model 362). As light source, a sulphur lamp (solar 1000), white light, 100 mW/cm^2 (measured with a powermeter at 530 nm) was used. Reduced light intensity was achieved using neutral density filters.

Layer thickness

Thickness of the films was measured by a Tencor P-10 profilometer.

Absorption spectra

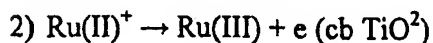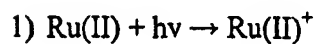Absorption spectra were taken by a Variant UV/Vis spectrometer.
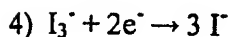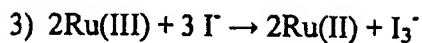

Example 3

The photovoltaic cell is fabricated by drop casting the ready made gel electrolyte on top of the dye-sensitised porous TiO$_2$ coated electrode, and sandwiched with a platinum back-electrode.

The layer thickness of the nanocrystalline TiO$_2$, is varied in the range of 2 to 20 µm, containing particles of 10 or 20 nm in diameter. The illuminated area of the cell is ca. 0.5 - 0.6 cm^2. As sensitiser dye cis-di(thiocyanato) bis (2,2'-bipyridyl-4,4'-dicarboxylate) ruthenium (II) tetrabutylammonium (Ru(bpy)TBA) is used.

The electron transfer and transport processes in the cell are schematically shown in figure 2. Light absorbed by the dye molecules injects electrons in to TiO$_2$ (t – 10^{-12} s) and holes into the Li/I$_2$ system (t – 10^{-8} s). At the Pt back-electrode, the resulting I$_3^-$ species will be reduced to I$^-$, undergoing the following redox reactions [D. Kuciauskas, M.S. Freund, H.B. Gray, J.R. Winkler, and N.S. Lewis, J. Phys. Chem. B 105 (2001) 392]

1) $Ru(II) + hv \rightarrow Ru(II)^+$

2) $Ru(II)^+ \rightarrow Ru(III) + e \ (cb \ TiO^2)$

3) $2Ru(III) + 3 I^- \rightarrow 2Ru(II) + I_3^-$

4) $I_3^- + 2e^- \rightarrow 3 I^-$

The iodide is used to reduce the oxidised dye. It also contributes the ionic charge transport, which is achieved by the I^-/I_3^- redox couple. The negative charge carrier in the electrolyte has the advantage to strongly reduce the probability of the recombination reactions with electrons injected into the porous TiO_2. The presence of mobile ions in the electrolyte, such as Li^+ from an inert salt like bistrifluoromethane sulfonimide lithium ($Li((CF_3SO_2)_2N)$), affects the charge transport and can further reduce the recombination reactions by screening photogenerated electrons and holes from each other and by surface adsorption of Li^+, giving a high amount of positive charge at the surface. A dipole is formed across the Helmholtz layer, which yields an electrical potential drop across the Helmholtz layer that helps to separate the charges and to reduce the recombination. A high amount of I^- gives a high photocurrent, the addition of an inert salt raises the photocurrent amplitude, though there is almost no photocurrent with only inert salt [A. Solbrand, A. Henningsson, S. Södergren, H. Lindström, A. Hagfeldt, and S.-E. Lindquist, J. Phys. Chem. B 1999, 103, 1078]

A schematic description of the processes in the cell is shown in Fig. 2A, wherein 1 denotes photon absorption, 2 denotes electron injection, 3 denotes dye reduction, 4 denotes I_3^- reduction, a and b electronic recombination, VB and CB denote valence band and conduction band, respectively. The relative positions of the energy levels are roughly to scale.

The right combination of all components in the cells is a crucial point. In general, the use of a semiconductor with larger band gap, and with low electron affinity in the electrolyte is favored, as well a semiconductor with hight density of states in the CB.

Example 4

Photochemical measurements of the polymer gel hybrid solar cells consisting of PEO polymer gel electrolyte and 7 μm porous TiO_2 layer of 10 nm particles, gave an open circuit voltage (V_{oc}) of 693 mV, short circuit current (J_{JC}) of 14.4 mA/cm^2, fill factor (FF) or 47 %, and an overall energy conversion efficiency (η) of 4.7 % with white light of Am1.5 (100 mW/cm^2, standard for solar cell characterisation). The I/V-curves are shown in figure 3.

A major factor limiting the energy conversion efficiencies is the low photovoltage. Here

charge recombination at the TiO_2 / electrolyte interface plays a significant role. Small molecules like derivatives of benzoic acid or pyridine, adsorb to TiO_2 and block the free interface, which results in a reduced recombination [J. Krüger, U. Bach, and M. Grätzel, Advanced Materials 12 (2000) 447, S.Y. Huang, G. Schlichthörl, A.J. Nozik, M. Grätzel and A.J. Frank, J. Phys. Chem. B. 1997, 101, 2576]. Adding tert.-butylpyridine to the polymer gel electrolyte improved both V_{oc} and η of the polymer gel hybrid solar cell significantly. The corresponding cells gave V_{oc} of 800 mV, J_{SC} of 16 mA/cm^2, FF of 55 %, and η of 7 % with 100 mW/cm^2 (also see Fig. 4).

A further important parameter in the dye-sensitised solar cells seems to be pore size, which is determined by the diameter of the nanocrystalline TiO_2 particles, and which also influences the penetration behaviour of the polymer gel electrolyte into the pores. To investigate this influence a paste was used containing particles of 20 nm diameters. The roughness of the layers consisting of the 20 nm particles is higher than the one of the 10 nm particles containing layer. In 4 µl porous TiO_2 layers, the pore size of the 20 nm particles containing layer is expected to be larger and the surface area is expected to be smaller. This should have an influence on the cell performance.

Photochemical measurement of a solar cell consisting of a 9 µl porous TiO_2 layer of 20 nm particle and tert.-butylpyridine at the interface showed V_{oc} of 800 mV, J_{SC} of 17.8 mA/cm^2, FF of 55 %, and η of 7.8 % with 100 mW/cm^2. Different from the Si-based solar cells, dye-sensitised TiO_2 solar cells do not show a linear dependence of η on the white light intensity. Depending on the electrolyte, they show a maximum in η around 20 mW/cm^2. The origin of this phenomena might be explained by an increase in the device serial resistance R_6, induced by a higher charge carrier density at the TiO_2 / electrolyte interface arising primarily from the limited ionic conductivity. Measurements with light intensity of 17 mW/cm^2 gave V_{oc} of 760 mV, J_{SC} of 4.33 mA/cm^2, FF of 70 % and η of 13.6 % (also see Fig. 5).

Mobility of the redox agent has an influence on the regeneration of the dye. To enable a fast regeneration, the iodide should be as mobile as possible. The size of the corresponding cation has an influence on the anion mobility; the larger the cation, the higher the dissociation, the higher the mobility of I^-. Using NaI rather than LiI resulted in an increase in FF and therefore in η. Photochemical measurement of a solar cell consisting of a 9 µm porous TiO_2 layer of 20 nm particle and tert-butylpyridine showed V_{oc} of 765 mV, J_{sc} of 17.8 mA/cm^2, FF of 68%, and η of 9.2% with 100 mW/cm^2. Measurements with light intensity of 33 mW/cm^2 gave V_{oc}

of 705 mV, J_{sc} of 9 mA/cm^2, FF of 73% and η of 14.1% (Fig. 6 and 6A). Those values are, as of the filing date of this application, to the knowledge of the inventors, the best reported ever for polymer gel hybrid solar cells.

The preparation techniques applied in the type of solar cell described in the present application can be used for large area devices. To keep the serial resistant as small as possille, small areas are of advantage. Single cells may have an area of 0.1 - 100 cm^2, preferably 0.1 –30 cm^2, more preferably 0.1 - 10 cm^2, even more preferably 0.1 - 5.0 cm^2, most preferably 0.1 - 1.0 cm^2. In addition, arrays of solar cells, either all in serial connection, or partly in parallel and serial connection or all in parallel connection are envisioned. The applied design depends on the requirements - higher V_{oc} or J_{SC}.

The features of the present invention disclosed in the specification, the claims and/or the drawings may both separately and any combination thereof be material for realizing the invention in various forms.

A polymer gel hybrid solar cell

Claims

1. A polymer gel hybrid solar cell comprising a polymer gel electrolyte, wherein the polymer gel electrolyte comprises a polymer, selected from the group comprising homopolymers and copolymers.

2. The polymer gel hybrid solar cell according to claim 1, wherein the homopolymer is linear or non-linear.

3. The polymer gel hybrid solar cell according to claim 1, wherein the copolymer is selected from the group comprising statistical copolymers, random copolymers, alternating copolymers, block-copolymers and graft copolymers.

4. The polymer gel hybrid solar cell according to any of the foregoing claims, wherein the polymer is a linear polymer.

5. The polymer gel hybrid solar cell according to any of the foregoing claims, wherein the polymer is crosslinked.

6. The polymer gel hybrid solar cell according to claim 5, wherein the polymer is not covalently crosslinked.

7. The polymer gel hybrid solar cell according to claims 5 - 6, wherein the polymer is physically crosslinked.

8. The polymer gel hybrid solar cell according to any of the foregoing claims, wherein the polymer has a $M_w > 90,000$.

9. The polymer gel hybrid solar cell according to claim 8, wherein the polymer has a $M_w >$ 200,000.

10. The polymer gel hybrid solar cell according to claim 8, wherein the polymer has a $M_w >$ 400,000.

11. The polymer gel hybrid solar cell according to any of the foregoing claims, wherein the polymer constitutes 1 – 10 wt% of the polymer gel electrolyte.

12. The polymer gel hybrid solar cell according to claim 11, wherein the polymer constitutes 1 – 5 wt% of the polymer gel electrolyte.

13. The polymer gel hybrid solar cell according to any of the foregoing claims, wherein the polymer gel electrolyte has an ionic conductivity $> 1 \times 10^{-6}$ S/cm, the value being measured without a redox couple being present in the polymer gel electrolyte.

14. The polymer gel hybrid solar cell according to claim 13, wherein the polymer gel electrolyte has an ionic conductivity $> 1 \times 10^{-3}$ S/cm.

15. The polymer gel hybrid solar cell according to any of the foregoing claims, wherein the polymer gel electrolyte further comprises a base and/or a radical scavenger and/or a complexing agent and/or a pinhole-filler and/or a compound reducing the charge recombination.

16. The polymer gel hybrid solar cell according to claim 15 and/or any of the foregoing claims, wherein the polymer gel electrolyte further comprises an amine.

17. The polymer gel hybrid solar cell according to claim 16, wherein the amine is a pyridine or a pyridine derivative selected from the group comprising pyridine, 4-tert-butylpyridine, 2-vinylpyridine, and poly(2-vinylpyridine)

18. The polymer gel hybrid solar cell according to claim 15, wherein the base/radical scavenger/ complexing agent/pinhole-filler/compound reducing the charge recombination is a compound selected from the group comprising compounds having one or several carboxy

groups, compounds having one or several amine groups, compounds having one or several carboxy and one or several amine groups, and compounds having free electron lone pairs.

19. The polymer gel hybrid solar cell according to any of the foregoing claims, wherein the polymer gel electrolyte further comprises a redox couple.

20. The polymer gel hybrid solar cell according to claim 19, wherein the redox couple has a low probability to perform recombination reactions with electrons injected into the negatively charged molecules of the electron transport layer.

21. The polymer gel hybrid solar cell according to claim 20, wherein the redox couple is I^-/I_3^-.

22. The polymer gel hybrid solar cell according to claim 21, wherein the redox couple is I^-/I_3^- with the counterion C of I^- being selected from the group comprising Li, Na, K, tetrabutylammonium, Cs and DMPI (molten salt).

23. The polymer gel hybrid solar cell according to any of the foregoing claims, wherein the polymer gel electrolyte further comprises a salt.

24. The polymer gel hybrid solar cell according to claim 23, wherein the salt is a redox inert salt.

25. The polymer gel hybrid solar cell according to claim 24, wherein the redox inert salt is $Li(CF_3SO_2)_2N$.

26. The polymer gel hybrid solar cell according to any of the foregoing claims, wherein the polymer gel electrolyte further comprises at least one solvent selected from the group comprising propylene carbonate, ethylene carbonate, dimethyl carbonate and acetonitrile.

27. The polymer gel hybrid solar cell according to any of the foregoing claims, wherein the polymer gel electrolyte is ionically and/or electronically conductive.

28. The polymer gel hybrid solar cell according to any of the foregoing claims, wherein the polymer gel electrolyte is selected from the group comprising:

- polyethylene oxide, $LiClO_4$, propylene carbonate and/or ethylene carbonate,
- polyethylene oxide, NH_4ClO_4, propylene carbonate and/or ethylene carbonate,
- polyethylene oxide and/or polymethylmethacrylate, $LiClO_4$, propylene carbonate and/or ethylene carbonate,
- polyacrylonitrile, Li- and/or Mg trifluoromethanesulfonate, propylene carbonate and/or ethylene carbonate,
- polyethylene oxide and poly(2-vinylpyridine), $LiClO_4$, 7,7,8,8-tetracyano-1,4-quinodimethane and/or tetracyanoethylene (TCNE),
- polyethylene oxide and polyaniline, $Li(CF_3SO_2)_2N$ and $H(CF_3SO_2)_2N$,
- polyaniline grafted with poly(ethyleneoxy)carboxylate,
- polyethylene oxide and poly(3,4-ethylenedioxythiophene)-polystyrenesulfonate (PEDOT-PSS).

29. The polymer gel hybrid solar cell according to any of the foregoing claims, which is dye-sensitised.

30. The polymer gel hybrid solar cell according to claim 29, wherein the dye is a ruthenium complex.

31. The polymer gel hybrid solar cell according to any of the foregoing claims, wherein the polymer gel electrolyte further comprises nanoparticles.

32. The polymer gel hybrid solar cell according to claim 31, wherein the nanoparticles have an average size in the range from 2 nm – 25 nm.

33. The polymer gel hybrid solar cell according to any of claims 31 – 32, wherein the nano-particles are formed of a semiconductor material.

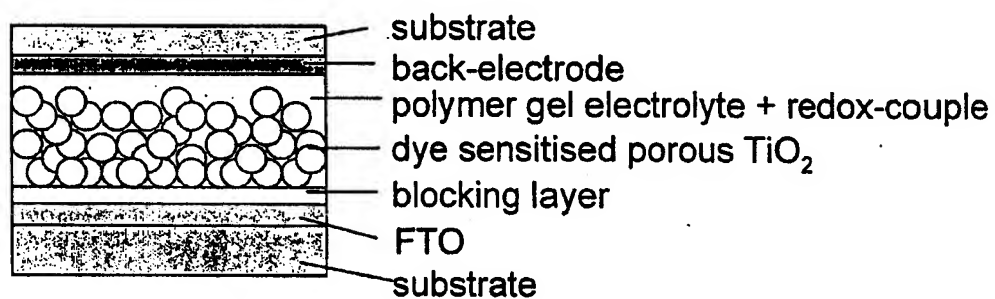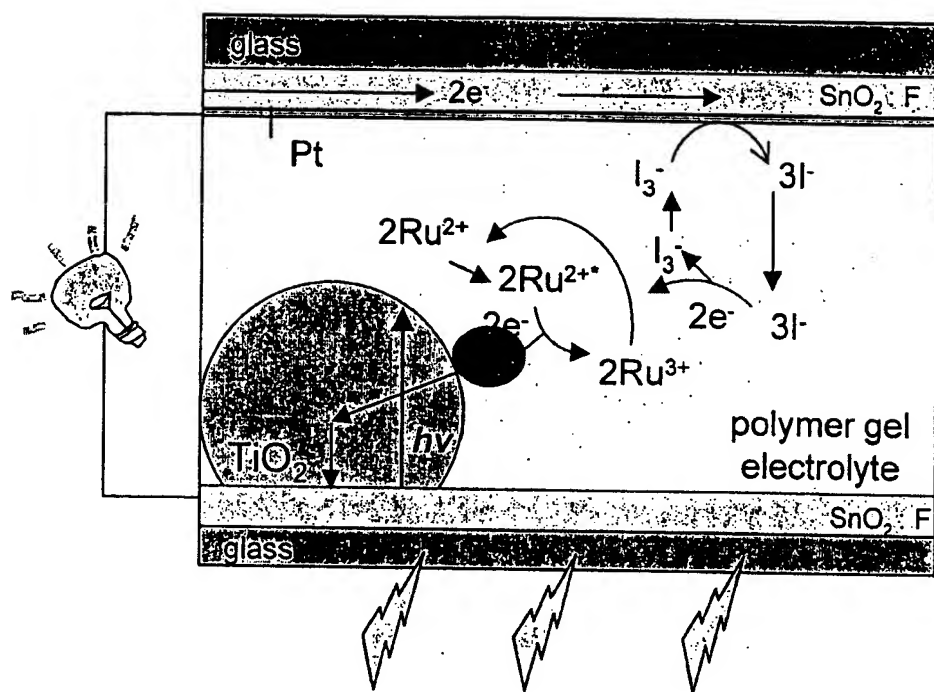34. An array of polymer gel hybrid solar cells according to any of the foregoing claims.

- substrate
- back-electrode
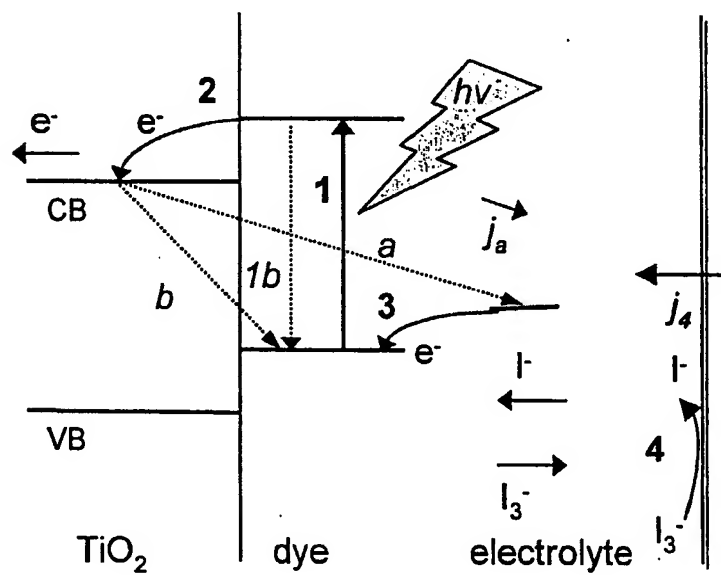- polymer gel electrolyte + redox-couple
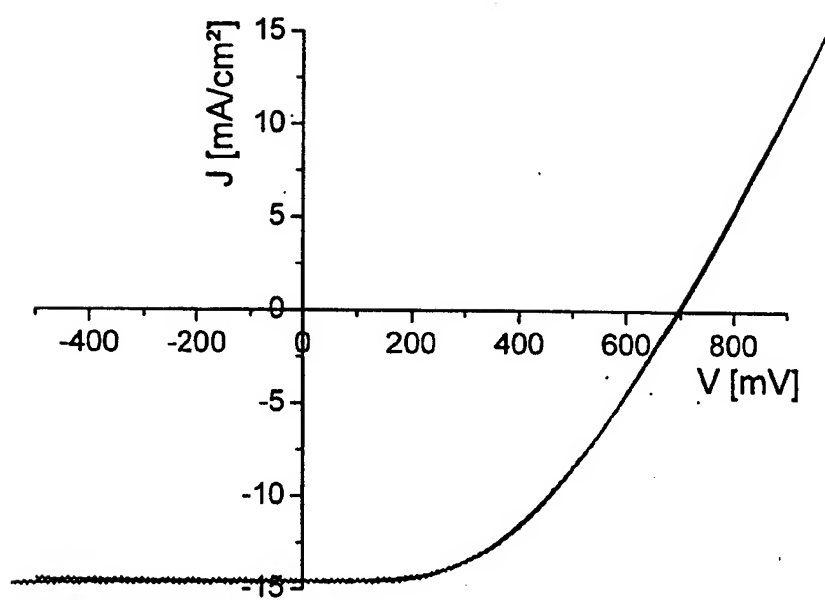- dye sensitised porous TiO_2
- blocking layer
- FTO
- substrate

Fig 1

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Fig 2

Fig 2A

Fig 3
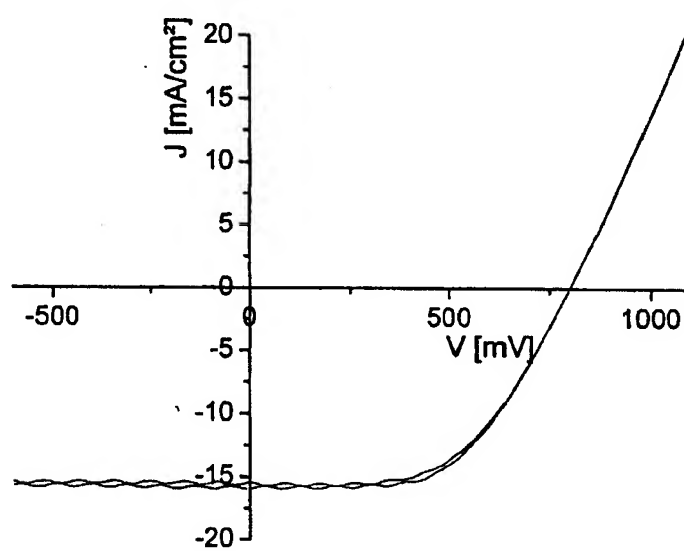
Fig 4

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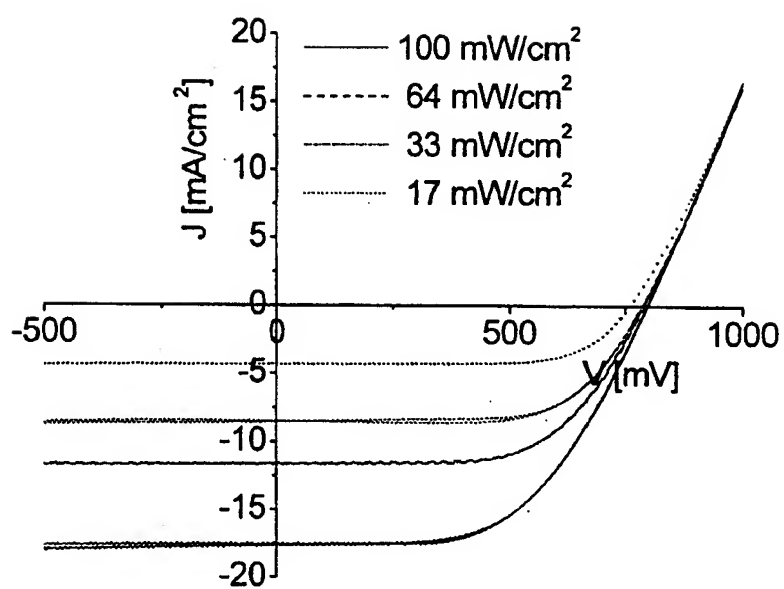
Fig 5

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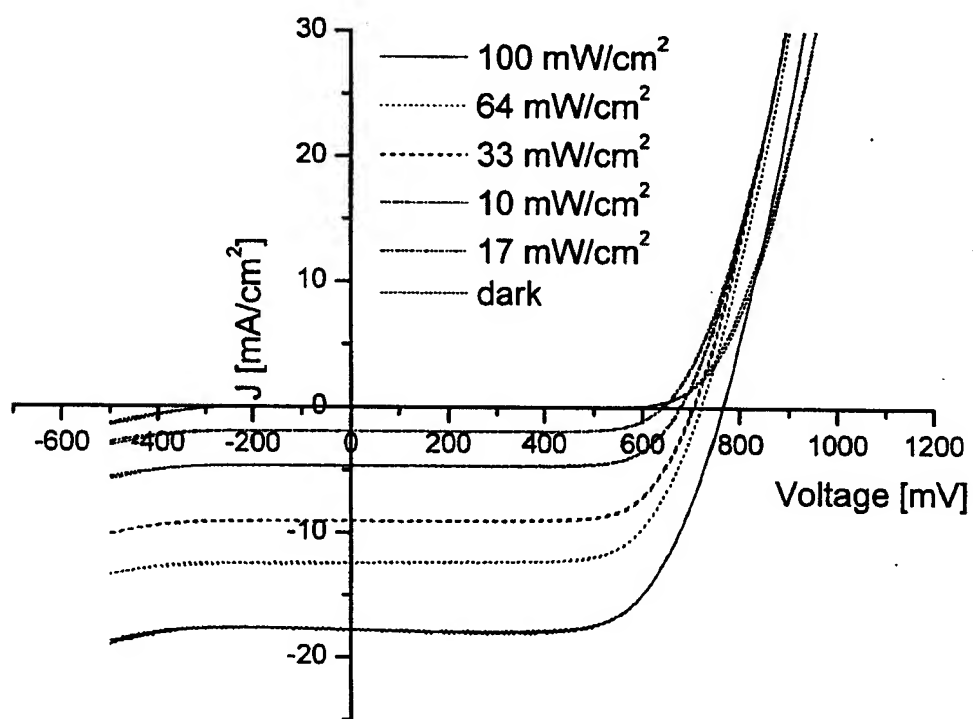
Fig 6

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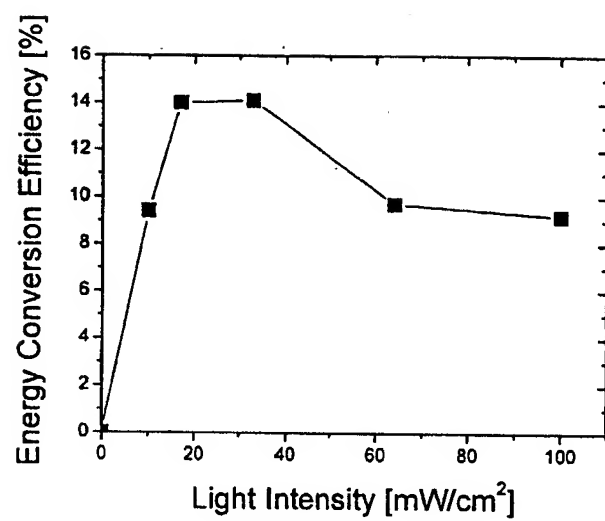
Fig 6A

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7   H01G9/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7   H01G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, INSPEC, PAJ, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category°	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 43 27 114 A (QUINTEN WERNER) 30 March 1995 (1995-03-30) claims 1,2 ---	1-5,11, 12,15, 16,18-27
X	BANDARA L R A K ET AL: "DYE SENSITIZED PHOTOELECTROCHEMICAL SOLAR CELLS WITH PEO BASED SOLID POLYMER ELECTROLYTES" WORLD SCIENTIFIC, SINGAPORE, IO, 29 November 1998 (1998-11-29), pages 493-498, XP000826871	1-10, 19-23, 26-30
Y	the whole document ---	15-17, 24,25
Y	WO 99 28292 A (ARMAND MICHEL ;UNIV MONTREAL (CA); ACEP INC (CA); CHOQUETTE YVES () 10 June 1999 (1999-06-10) the whole document ---	24,25
	-/--	

[X] Further documents are listed in the continuation of box C.   [X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
28 March 2003	04/04/2003

Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Authorized officer Königstein, C

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
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